Summary

Thesis outline

Speleothems are carbonate concretes formed in the stable and humid environment of cave systems. The most common speleothems are stalagmites and stalactites. This research focuses on the climate information recorded in speleothems and specifically in stalagmites. Many land and ocean based climate reconstructions are derived from subtle variations in the stable isotope composition of oxygen. In the natural environment, the element oxygen consists of three stable isotopes namely $^{16}\text{O}$, $^{17}\text{O}$ and $^{18}\text{O}$. An isotope has a different amount of neutrons but always the same amount of protons as other isotopes of the same element. Due to various physical and chemical processes, the lighter isotope ($^{16}\text{O}$, fewer neutrons) will react differently from the heavy isotope ($^{18}\text{O}$, more neutrons). This results in changes in the ratio of the $^{16}\text{O}$ and $^{18}\text{O}$ isotopes in the natural environment. Ratios of the different isotopes of the elements oxygen, carbon and hydrogen can all provide useful information about the climate of the past, for example reconstructing past changes in temperature and rainfall patterns. Important climatic information can be extracted from (rain) water using these various isotopic ratios, however fossil rainwater is scarce and mainly available as ice in glaciers and polar ice caps. Climate research based on ice cores form an important basis of our understanding of the Quaternary climate, because this fossil water can be analysed. A disadvantage is that ice cores are geographically limited to the polar climates on Earth.

Temperature information is also recorded in the oxygen isotope composition of carbonate (calcite/aragonite), from which cave stalagmites are composed. The ratio between oxygen isotopes ($^{18}\text{O}/^{16}\text{O}$) is temperature dependent, and therefore will provide temperature information at time of carbonate deposition. However, for paleotemperature calculations we require both the oxygen isotope ratio of the speleothem carbonate and the oxygen isotope composition of the cave water (i.e. fossil water) at the time of deposition. In the speleothem carbonate, a small amount of cave drip water (fossil water) is still present, so-called fluid inclusions. If the isotope composition of this 'fossil' drip water can be measured, the isotope composition of the original drip water is known and in combination with the oxygen isotope composition of the speleothem carbonate, the temperature at the time of deposition can be calculated.

This research details the first speleothem records of Holocene climate changes from the Peruvian Andes. For these climate reconstructions we focused on stable isotope and trace element analyses of speleothem carbonate. To better quantify variability in temperature and rainfall from these proxy records, we further developed a technique for the stable isotope analysis of fossil 'drip water' trapped in small cavities (fluid inclusions) of the speleothem carbonate. The hypothesis is that the combination of fluid inclusion stable isotope data with associated speleothem carbonate stable isotope data enables the calculation of true paleotemperatures.
The thesis is divided in two parts. The first is technically orientated (chapters 2 - 5) and presents the U-Th dating technique (chapter 2), a monitoring study of a Peruvian cave (chapter 3) and two different techniques to extract and measure the isotope composition of speleothem inclusion water (chapter 4 & 5). These techniques are then applied to stalagmites collected from three caves in Peru. The results are presented in chapters 6 – 9. Chapter 6 & 7 present the climate interpretation of two lowland caves from the Amazon basin, whereas chapter 8 presents the first climate record of an Andean highland stalagmite. Chapter 9 compares the fluid inclusion data collected from low- and highland Peru with a simple distillation model.

Chapter 1: Introduction
General information about the climate of South America and the formation of stalagmites.

Chapter 2: Uranium-series dating method applied on speleothems
The Uranium-series dating technique is complex and fundamental for speleothem-based climate research because it provides an independent, robust age framework. All of the collected Peruvian stalagmites were U/Th age dated at the Vrije Universiteit Amsterdam (VUA) and so we begin by detailing the methods used. Besides an age framework, low resolution stable isotope records were also produced. Based on the combined age framework and stable isotope data, we selected the most suitable material to investigate the Holocene period. The collected and dated speleothems for this pilot study are presented in this chapter, but no further detail is given.

Chapter 3: Seasonal environmental monitoring results from a cave in Peruvian Amazonia
During September 2003 and 2004, between two fieldwork periods a monitoring experiment was carried out in Cueva de las Lechuzas. The monitored data consists of stable isotope and trace element measurements on collected water samples in combination with continuously monitored temperature and drip rates at specific locations within the cave. This experiment was set up to investigate the cave environment and its response to seasonal climate changes and shows the complex and dynamic response cave hydrology to outside precipitation.

Chapter 4: A continuous-flow crushing device for on-line $\delta^2$H analysis of fluid inclusion water in speleothems
A key theme in this thesis is the development of a method to accurately measure the stable isotope ratio ($\delta^2$H) of fluid inclusion water from speleothem calcite. This thesis describes two independent techniques for fluid inclusion extraction in chapters 4 and 5 respectively. Chapter 4 describes a new method developed at the VUA, which makes it possible to extract inclusion water from speleothem calcite and accurately measure its stable isotope composition. This is a major technical achievement for fluid inclusions extraction and measurements and offers new possibilities in speleothem climate research (as is published in chapters 6, 7, 8 and 9).
Chapter 5: Water release patterns of heated speleothem calcite and hydrogen isotope composition of fluid inclusions

Chapter 5 describes the process of water release when speleothem calcite is heated up to \( \sim 900^\circ C \). Observations show that water is released during the break down of the calcite crystals and during the decomposition of the calcite to lime. The two stages of water release were separately measured in terms of \( \delta^2 H \) composition and a small difference was observed. The advantage of this technique is that the water yield is higher in comparison to the 'crushing' technique. The disadvantage is that oxygen isotopes become unreliable after decomposition of calcite to lime and consequently only hydrogen isotope data can be collected. This work is performed in cooperation with the 'Laboratoire des Sciences du Climat et l'Environnement' (France) with resulted in a co-author paper.

Chapter 6: Fossil dripwater in stalagmites reveals Holocene temperature and rainfall variations in Amazonia

A speleothem record covering the complete Holocene provides an insight in Holocene temperature and rainfall variation in Amazonia. The temperature variations calculated remain small throughout the Holocene, suggesting that rainfall variation is the dominant climatic factor in Amazonia. In phase isotope records of fluid inclusion and speleothem calcite suggest that rainfall variation are solar insolation driven.

Chapter 7: High resolution stable isotope and trace element speleothem record of the last \( \sim 5000 \) year, Cueva de las Lechuzas, lowland Peruvian Amazonia

A stalagmite from Cueva de las Lechuzas is measured for stable isotope composition and trace element concentrations. This record covering the late Holocene, shows a distinct centennial-scale cyclicity, visible in both oxygen and carbon isotopes of the speleothem calcite and also in trace element concentrations. The pattern is consistent and in phase for all measured proxies and is interpreted as being drip rate driven. As the cave hydrological reservoir is fed by water of meteoric origin, the data is sensitive to changes in the amount of rainfall and reflects rainfall variation for the last 5000 years.

Chapter 8: Climate reconstruction of the Andean highland based on a late Holocene speleothem from Gruta de Huagapo

A stalagmite from Gruta de Huagapo located at 3572 meters above sealevel is investigated. Stable isotope and trace element analyses of the speleothem calcite reconstruct variations in precipitation. Combined stable isotope analyses on fluid inclusion water and speleothem calcite reveal temperature changes over the last 5000 year. Cooler temperature coincide with periods of dryer conditions, while warmer temperatures show signs of increased rainfall.

Chapter 9: Late Holocene rainwater stable isotope fractionation patterns as evidenced in fluid inclusions from stalagmites and snow from ice cores in an altitudinal transect over the Andes mountain chain

The possibility to directly measure the stable isotope composition of fossil rain water provides the opportunity to create an altitudinal profile of rainwater isotope composition across
the Andean mountain chain. Two lowland speleothem records are compared with a highland
speleothem record and ultimately with the Andean Ice cores of Queleccaya and Huascaran.
All records consist of stable isotope data, representative for fossil rainwater. These data are
compared with a simple Rayleigh distillation model.